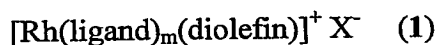


CLAIMS

1. A process for preparation and isolation of a non-amorphous cationic rhodium complex of formula (1), wherein ligand represents an enantiomerically enriched organic compound possessing one or two ligating phosphorus atoms, and wherein m = 2 when the ligand is monodentate and m = 1 when the ligand is bidentate, which comprises the following steps:

- (a) Dissolution of Rh(diolefin)(acac) in one or more ethereal solvents;
- (b) Addition of a fluorinated non-mineral acid HX and alcohol solvent or alcohol-containing solvent mixture, either simultaneously or sequentially, to form a soluble solvated complex of rhodium with one or more of the reaction solvents;
- (c) Addition of the ligand, either in solution in an organic solvent or neat;
- (d) Collection of the crystalline precipitate of complex (1).



2. A process according to claim 1, wherein step (b) comprises simultaneous addition of HX and alcohol solvent or alcohol-containing solvent mixture.
3. A process according to claim 2, wherein step (b) comprises addition of HX as a solution in an alcohol solvent or alcohol-containing solvent mixture.
4. A process according to claim 1, wherein step (b) comprises sequential addition, in either order, of HX and alcohol solvent or alcohol-containing solvent mixture.
5. A process according to claim 1, wherein the diolefin is a cyclic diolefin.
6. A process according to claim 5, wherein the diolefin is either 1,5-cyclooctadiene (COD) or 2,5-norbornadiene (NBD).
7. A process according to claim 6, wherein the diolefin is COD.

8. A process according to claim 1, wherein diolefin represents two molecules of an olefin selected from the group consisting of ethylene and C<sub>5-10</sub> cycloalkenes.
9. A process according to claim 1, wherein HX is a perflourinated non-mineral acid.
- 5 10. A process according to claim 9, wherein HX is selected from the group consisting of HBF<sub>4</sub>, HPF<sub>6</sub>, HSbF<sub>6</sub> and CF<sub>3</sub>SO<sub>3</sub>H.
11. A process according to claim 10, wherein HX is HBF<sub>4</sub>.
- 10 12. A process according to claim 1, wherein ethereal solvents are selected from the group consisting of dialkyl ethers, tetrahydrofuran, 1,4-dioxane and 1,2-dimethoxyethane.
- 15 13. A process according to claim 12, wherein dialkyl ethers are selected from the group consisting of *t*-butyl methyl ether, diethyl ether, diisopropyl ether and di-*n*-butyl ether.
14. A process according to claim 13, wherein a dialkyl ether is in admixture with
- 20 tetrahydrofuran.
15. A process according to claim 14, wherein the ratio of dialkyl ether:tetrahydrofuran ranges from about 10:1 to about 1:1.
- 25 16. A process according to claim 15, wherein the ratio of dialkyl ether:tetrahydrofuran ranges from about 6:1 to about 2:1.
17. A process according to claim 16, wherein the dialkyl ether is *t*-butyl methyl ether.
- 30 18. A process according to claim 1, wherein the alcohol is a linear or branched C<sub>1-6</sub> alkanol.
19. A process according to claim 18, wherein the alkanol is selected from the group comprising methanol, ethanol, *n*-propanol, isopropanol, and 1-butanol.

20. A process according to claim 1, wherein the organic solution used for dissolution of ligand is selected from the group comprising ethereal solvents, non-polar hydrocarbon solvents and mixtures thereof.

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21. A process according to claim 1, wherein  $m = 1$ .

22. A process according to claim 21, wherein the ligand is a diphosphine.

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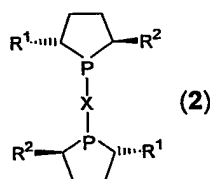
23. A process according to claim 22, wherein the diphosphine is a bisphosphacycle.

24. A process according to claim 23, wherein the bisphosphacycle is a bisphospholane.

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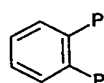
25. A process according to claim 24, wherein the bisphosphacycle is a bisphospholane according to formula (2), or the opposite enantiomer thereof, wherein X represents an organic or organometallic bridging radical,  $R^1$  and  $R^2$  are each independently H or an optionally substituted hydrocarbon group, provided that  $R^1$  and  $R^2$  are not both H, and the 3- and 4-positions of either or both phospholane rings optionally may be substituted with one or more non-interfering groups.

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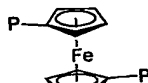
26. A process according to claim 25 wherein P-X-P in the bisphospholane is selected from a group consisting of formulae (3) to (8), each of which may be optionally substituted; n in (4) is in the range 0-5; X in (8) is either O or N-alkyl.



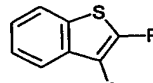
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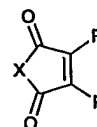
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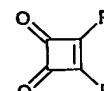
(5)



(6)



(7)



(8)

27. A process according to claim 26, wherein P-X-P is of formula (3).

28. A process according to claim 26, wherein P-X-P is of formula (4) and  $n = 1$ .

29. A process according to claim 26, wherein P-X-P is of formula (5).

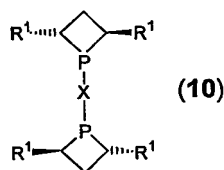
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30. A process according to claim 24, wherein the bisphosphacycle is a bisphospholane according to formula (9), the opposite enantiomer thereof and substituted analogues thereof.

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31. A process according to claim 23, wherein the bisphosphacycle is a bisphosphetane of formula (10), wherein X represents an organic or organometallic bridging radical,  $R^1$  and  $R^2$  are each independently H or an optionally substituted hydrocarbon group, provided that  $R^1$  and  $R^2$  are not both H, and the 3-position of either or both phosphetane rings optionally may be substituted with one or more non-interfering groups.

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32. A process according to claim 31, wherein X is 1,1'-ferrocenyl.

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33. A process according any of claims 25-29 or 31-32, wherein  $R^1$  and  $R^2$  are each independently  $C_{1-20}$  alkyl, aryl or aralkyl.

34. A process according to claim 33, wherein  $R^1 = R^2 = C_{1-20}$  alkyl.

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35. A process according to claim 34, wherein alkyl is selected from the group consisting of methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl and *t*-butyl.

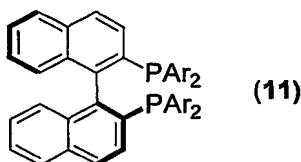
36. A process according to claim 33, wherein  $R^1 = R^2 =$  phenyl.

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37. A process according to claim 19, wherein the diphosphine is an atropisomeric diphosphine containing two  $P(Ar)_2$  groups, wherein Ar = phenyl, optionally substituted with one or more alkyl or alkoxy groups.

5 38. A process according to claim 32, wherein the diphosphine is a biaryldiphosphine.

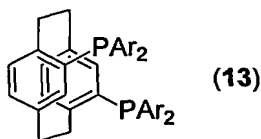
39. A process according to claim 33, wherein the biaryldiphosphine is a BINAP ligand of formula (11), or the opposite enantiomer thereof.



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40. A process according to claim 38, wherein the biaryl moiety is heteroaromatic.

15 41. A process according to claim 32, wherein the diphosphine is a PHANEPHOS ligand of formula (13), or the opposite enantiomer thereof.



20 42. A process according to claim 21, wherein at least one of the ligating phosphorus atoms in the ligand is covalently bonded to one or more heteroatom.

43. A process according to claim 42, wherein both ligating phosphorus atoms are covalently bonded to one or more heteroatoms.

25 44. A process according to claim 43, wherein the ligand is selected from the group consisting of bisphosphites, bisphosphinites, bisphosphonites and bisphosphoramidites.

45. A process according to claim 1, wherein  $m = 2$ .

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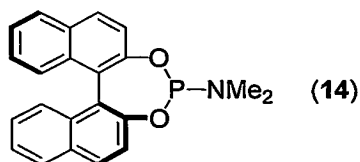
46. A process according to claim 45, wherein the ligand is a monophosphine.

47. A process according to claim 46, wherein the phosphine is a *P*-aryl phosphacycle.

5 48. A process according to claim 45, wherein the ligating phosphorus atom in the ligand is covalently bonded to one or more heteroatoms.

49. A process according to claim 48, wherein the ligand is a phosphoramidite.

10 50. A process according to claim 49, wherein the phosphoramidite is of formula (14) or the opposite enantiomer thereof.



15 51. A process according to claim 1, wherein the complex (1) is prepared directly from a ligand precursor containing one or more acid-labile hydroxyl protecting groups, which are removed during complex formation.

20 52. A process according to claim 1, wherein the complex (1) is obtained in a crystalline form.

53. A process according claim 1, wherein the complex (1) is stable to storage, under an inert atmosphere at ambient temperature, for at least three (3) days.

25 54. A process according the claim 1, wherein the ligand is enantiomerically enriched to at least 95% ee.

55. A process according the claim 54, wherein the ligand is enantiomerically enriched to at least 99% ee.

30 56. A process according to claim 55, wherein the ligand is enantiomerically pure.